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Time-temperature relations for ignition of explosives.

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FOR IGNITION OF EXPLOSIVES

by

Jack L. Carter

Lieutenant Commander
United States Navy

Submitted in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE
IN
CHEMISTRY

United States Naval Postgraduate School
Monterey, California

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ABSTRACT

The determination of explosion temperatures is of considerable importance from the viewpoint of both safety and the information which such studies may give as to energies necessary for explosion. An attempt has been made to improve the equipment and procedures employed in past studies for this purpose. The equipment is described, and the results and procedures are discussed in relation to pertinent parameters affecting the determinations.

The writer wishes to express his appreciation for the assistance given him by Professor J. E. Sinclair of the U. S. Naval Postgraduate School.

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1. Introduction.

Knowledge of the conditions for initiation of detonation is of great practical importance both from the viewpoint of causing detonation to occur when it is wanted, and also to prevent it from occurring when it is not wanted, namely during manufacture, storage, shipment, and handling in preparation for use. This problem has received a great deal of consideration, and many methods have been designed for its study. One of these methods, that of determining the temperature of ignition versus time is likewise of considerable importance for the same reasons noted above and is the subject with which this study will be concerned. The expression "temperature of ignition" as used in this study, means temperature at which decomposition becomes explosive in character.

The ignition temperature cannot be considered constant. Past studies have indicated a variance dependent upon numerous variables. (1, 2, 3, 4, and 5) Those most generally believed to have an affect on ignition temperature have been thoroughly investigated and will be the subject of considerable discussion in the body of this report.

Methods employed in the past studies referred to above have been numerous and no less varied than the results obtained and conclusions reported. One can find in any treatise on the subject in question, statements such as the following:

> At different places different machines and apparatus are used, and the numerical results differ in consequence from laboratory to laboratory. (1)

This very pertinent statement and the differences to which it refers constitute a major part of the justification for this study. An analysis of the advantages and disadvantages of the different methods was necessarily made and will be discussed elsewhere in the report.

Thus the overall purpose of this study is to design and fabricate a device or system which will embody those advantages found to exist in previous methods and to alleviate those disadvantages or erroneous conclusions and assumptions determined to exist in these same past studies.

Success in the primary objective will permit, possibly, an investigation of perhaps more fundamental factors or properties involved in expressions relating to thermal sensitivity of explosives. Specifically it appears most desirable to appraise the feasibility of evaluating the energy necessary to induce ignition.

2. Investigation of parameters.

The subject of parameters is in itself a subject demanding careful and extensive analysis. One must clearly define a parameter for the particular method employed. Clarity and completeness of definition is essential for reasons as vital as they may be obvious. Every effort must be made to understand the existence and effect of each factor that does in fact affect the determinations. It is unlikely that a mere knowledge of relative effects of various parameters is sufficient in that such information tends to encourage the questionable practice of canceling consideration of those parameters which appear to counteract the effects of one another. When working with explosives, one seldom enjoys linear or proportional, and not always predictable relationships. By the same token, equal attention is necessary in elimination of all non-parameters to avoid nuisance problems and the attendant sacrifice in simplicity of machine and method. The results of this phase of the work produced the following parameters:

(1) Sample insulation

(2) Rate of heating

(3) Time sample is subjected to a given temperature

(4) Temperature to which sample is subjected

(5) Nature of sample

(6) Rate of heat loss

(7) Nature of surrounding medium

(8) Frequency of temperature recordings

(9) Position, with respect to sample, where temperature is taken.

Sample insulation:

This refers to the manner in which the sample is contained or pack-

aged during the period it is being subjected to heating. In some cases, where the uncontained sample is applied directly to a heat source, sample insulation would be a function only of the heat transfer and film coefficients of the heat source and explosive sample. Most frequently the sample is contained in some manner, usually a capsule of either copper, iron, or glass. In general, copper has received widest use of the three for various reasons. Its ready availability in a useable form, such as the shells for electric and non-electric detonators, undoubtedly represents a major advantage and justification for its application in the less complex and more direct methods to be discussed later. Copper containers are reuseable, an advantage for obvious reasons and at the same time a disadvantage in that considerable care must be exercised to insure absolute cleanliness and absence of metallic oxide films so that consistent and efficient heat conduction may be obtained in the interest of reproducible results. This calls for extensive sand papering and cleaning before and after all test runs. The excellent heat conductivity of copper is of course the major advantage and reason for its wide use. Rapid conduction of heat is essential to the success of any method of temperature versus time study wherein the assumption is made that the temperature of the heat bath is essentially that of the explosive sample at the time of ignition. A thorough analysis of this assumption will constitute a major portion of this project.

Glass capsules or containers have been used to a degree in some earlier studies, but wider application has been definitely limited, due primarily to poor heat conductivity properties. Where poor heat conduction is acknowledged, as in the case of glass, one is truly hard pressed to accept the general assumption that the heat bath temperature

is comparable to sample temperature. Aside from this very real disadvantage in those cases where only bath temperature is recorded, glass affords the user several worthwhile advantages, namely: cleanliness and oxide coatings are no longer a problem; thus heat transfer, though certainly not negligible, can be made constant for all tests by simply insuring uniformity of the glass container as to size, thickness, and type of glass. This represents a most desirable factor in the quest for reproducibility of results. Obviously, glass capsules cannot be reused and may present problems in the physical fabrication or design of equipment. However the relative ease with which glass may be formed and shaped, in addition to ready availability in a wide variety of capsule shapes and sizes, would seem to more than offset the usual design problems due to the fragile properties of glass.

For comparison purposes the following table lists temperatures of ignition and associated times for various explosives. (1, 5)

	Temp. raised 20 C° per minute		Explosion occurring in exactly 5 secs.	
EXPLOSIVE	GLASS	IRON	IRON	COPPER
Lead Azide	338	337	350	340
Merc. Fulminate	175	166	205	210
Lead Styphnate	276	275	268	282

These data have been tabulated here to indicate the close correlation of results that may be obtained regardless of the container employed. Though only three explosives have been listed, the variations shown are typical of results obtained for the great majority of explosives subjected to this type of test.

It may therefore be assumed that a decision to utilize one or another type of sample container need only satisfy physical design or fabrication requirements. Thus reproducible and consistent results may be obtained and considered independent of the type of material used

for sample insulation.

Period of time sample is subjected to a given temperature:

The effect this so-called parameter has upon the observed temperature of ignition has received considerable attention from the majority of authors concerned with studies of this nature. In general the conclusions reached by these authors tend to redesignate this time period. That is, rather than viewing it as a parameter they chose to regard it as the ultimate time lag they wish to measure and record. In so doing, it was in all cases necessary to assume that heat conduction was essentially instantaneous. Thus the recorded temperature of the explosive sample was considered to be the same as the heat source and this time interval thus became the time lag necessary for the sample to ignite at a constant temperature. These rather broad assumptions were necessary and sufficient to permit an evaluation of the energy of activation based upon reaction rate kinetics and heat balance equations. The final equation in simple form is as follows:

$$\log t = /RT_o + B$$

This equation is generally recognized as the appropriate relationship governing the time lag t, prior to explosion after heating to a temperature, $T_o(^oK)$. The derivation is given in Appendix II.

Rate of heating:

It is interesting to note that rate of heating is frequently mentioned by many authors as a parameter having considerable influence upon the temperature of ignition and the inherent time lag. The rate of heating of the sample is of course a direct function of the temperature to which the sample is exposed, the insulation of the sample, and, in some cases, the degree of self-heating occurring within the sample. Recognizing these facts, one is faced with an apparent contradiction

when the same authors follow with assumptions concerning instantaneous heat transfer. Intuitively, one expects an increase in the rate of heating to reduce the time required for ignition at a given temperature or conversely, to reduce the temperature of ignition at a given time. It is anticipated that the equipment and procedures to be employed in this project will substantiate this supposition.

Temperature to which sample is subjected:

This is a parameter in itself dependent upon underlying assumptions and procedures involved in the study. In the instance where this temperature is taken to be the temperature of ignition, its effect as a parameter will be restricted to the influence it will have on lag time alone. Herein an inverse relationship will exist as in the case of rate of heating. On the other hand, if, as this writer suspects, heat transfer may not in fact be instantaneous, then the temperature to which the sample is subjected will play a far more complex role. It would be expected that variations in this temperature would not only affect lag time but also the actual temperature of ignition by virtue of the inherent variations in rate of heating. The non-linearity of heat transfer rate with respect to temperature would thus introduce comparable non-linear time and temperature results. Equipment design and procedures was directed specifically toward clarification of this point. Clearly, to accomplish this, it shall be necessary to secure a more precise indication of sample temperature.

Nature of sample:

Recognizing that an important requirement is the design of laboratory scale equipment, sample size is immediately limited to very small quantities. Experience indicates the quantities in question should not

exceed 40 to 50 mg. to be consistent with general laboratory safety and particularly for simplicity in equipment design and procedures. Tests were conducted which indicate results are reproducible and independent of sample size up to 15 mg. Thus the proper sample size to use will be a design parameter which will be determined and tabulated with final results. Sample condition with respect to dryness has a definite influence on accuracy and reproducibility of results. It has been determined that a minimum 24 hour drying period in vacuum oven type apparatus is essential for all explosive samples. In general the explosives used in this project were standard commercial grades.

Rate of heat loss:

Referring to the simplified notation form of the heat balance equation given in Appendix II, the heat loss (F), by the explosive sample during the time interval is a low exponential function of temperature. The thermal conduction part of (F), for example, follows Newton's law, in which the heat loss is proportional to the thermal gradient. The radiation component of (F) follows the Stefan-Boltzman T^4 law. As temperature increases, the increase in (F) is however much less important than is the accumulation of heat (G) in the sample and for this reason is generally neglected as is shown in the derivation. It would appear nevertheless as further justification for a design which more accurately determines the actual temperature of the explosive sample, thus overcoming yet another possible error in the final determination.

Nature of surrounding medium:

Only in highly complex methods such as those employed by Robertson (2) and Yoffe (3), where an attempt is made to maintain isothermal conditions does the nature of the surrounding medium become significant. In these

cases the surrounding medium includes the atmosphere as well as the heat bath. Here atmospheres are controlled and facilities are included for collecting and analyzing the gases generated in decomposition. Where consideration of surrounding medium is restricted to the bath or heat source, the matter is greatly simplified. It can be reduced, in fact, to a design parameter where choice of material depends upon availability and procedure. The material must necessarily possess a low melting point, general stability over a wide temperature range with respect to composition, and a high boiling point.

Frequency of temperature recordings:

The frequency of temperature recording has an obvious and direct relationship to accuracy and reproducibility of data regardless of the method used. It can be readily appreciated that a procedure wherein a continuous record of temperature is obtained would possess marked advantages over intermittent recording methods. The final equipment design can best accomplish this aim through utilization of thermocouples in conjunction with continuous-operation pen-recording equipment.

Position with respect to sample where temperature is taken:

This factor represents a source of considerable variation in results reported by various sources. In virtually every case the temperature was taken by thermometer or thermocouple but always the temperature was that of the heat bath. Any method which continues to incorporate this feature in its design can do little more than contribute further data of comparable variation and questionable value. This parameter, like others mentioned previously, seems to demand a method to alleviate the problem of doubtful temperature data.

3. Equipment design and procedure.

The approach to the final design and operating procedures adopted can best be described as emanating from "trial and error" technique. Trials were based on investigation and review of previous methods and availability of materials. However, conclusions drawn from the foregoing analysis of parameters were the primary criteria.

The equipment consists essentially of four basic components:

(1) A heat source

(2) Sample container and immersion apparatus

(3) Timing system

(4) Temperature recording system

The design and ultimate fabrication of each component will be discussed separately.

Heat source:

This component has taken numerous forms in past studies. In the simpler systems the method usually consisted of a single bath containing some molten material such as Wood's metal. The container was normally metallic and cylindrical, approximately two inches deep and five inches in diameter. The container and a resistance wire heating element wrapped around it were enclosed in a suitable insulating material. A variable transformer was normally included to provide accurate heat regulation to give different temperatures. Such a method is quite satisfactory but lacks the versatility offered by a multiple bath bar type apparatus. The bar, as pictured in appendix III, consists of a solid cylindrical aluminum rod, three inches in diameter and 20½ inches in length. Ten holes were drilled into the bar one and one-half inch between centers. Each hole is one inch in diameter and one and one-half inches deep. An 11th

hole, two inches in diameter was drilled into the bar as a reservoir and is joined to the other holes by a longitudinal tap hole at the base of each. The purpose of the reservoir is to maintain a constant level of bath material in each hole. At one end of the aluminum bar is affixed a heating unit consisting of a resistance wire heating element wrapped around a solid brass cylinder. Configuration of the brass cylinder is such that a protective flange exists between the heating element and the aluminum rod. The outside end of the brass cylinder is threaded and a collar provided to allow compression of the spiralled heating element so as to improve heat transfer to the cylinder. The resistance of the heating coil is 6.6 ohms and at 115 volts allows 17.5 amperes to flow.

The bath medium used in this study is a mixture of nitrate-nitrite salts called "Tempering 350 Pink," a product of Holden Metallurgical Products. This material melts at 146°C, and possesses an operating range of from 163°C to 593°C. It further offers satisfactory and stable electrical conductivity over the necessary temperature range.

The entire bar assembly is mounted inside a rectangular box of Maronite insulation sheeting. The latter is one inch thick, six inches high and 28 inches long.

A variable transformer is included in the heating circuit to permit current regulation necessary for various temperature gradients. Appendix IV lists gradients characteristic of the bar assembly for various voltages.

Sample container and immersion apparatus:

A metallic container was considered undesirable for the reasons previously discussed. In addition a frangible container was called for to facilitate incorporation of the anticipated timing system to be discussed

subsequently. It was found that four inch long Kimax melting point capillary tubes were ideally suited for the intended application. A general radio type jack was modified to provide a mounting for the melting point tube and a means of attaching the tube to a vertically sliding bar. This and the complete immersion apparatus are depicted in Appendix V. The slide itself is secured at the top to the armature of a 24 volt DC solenoid which, when energized, retains the slide in the upward position, thereby permitting the sample tube to be centered above the desired bath. This system affords the desirable feature of remote actuation of the sample immersion apparatus by interrupting the electrical circuit and deenergizing the solenoid. Thus the slide bar falls to a predetermined position, immersing the sample tube in the heat bath. Electrical control of the immersion apparatus in addition permits syncronization with the timing system. The entire assembly includes an inverted U shaped support mounted on rails on either side of, and parallel to, the heat bar.

Timing system:

Timing techniques employed in previous studies were usually electrically operated, though a few relied solely upon manually operated stop watches. The electrical systems were actuated by completion of an electrical circuit to a timing device whenever the metallic sample container made contact with the conducting solution used as a heat bath. Termination of the timing cycle resulted from the interruption of the electrical circuit in some manner. This was most often accomplished by utilizing the pressure exerted by the gases generated upon detonation or ignition to displace a cap or lever affixed to the top of the sample container. An inherent drawback in this method is the fact that appreciable quantities of sample were required to generate sufficient

pressure to accomplish a positive break in the timing circuit. Thus the feasibility of making, rather than breaking a circuit was investigated. After considerable trial and error, a very satisfactory method has been developed wherein a very fine copper wire is exposed in the bath when sample detonation fractures the melting point tube. In this way a circuit is completed from a 24 volt DC source through a relay, the copper wire, the bath medium, and the aluminum bar to ground. A schematic of this system appears in Appendix VI. The actuation of the relay in this manner breaks the power circuit to the timer and terminates the timing cycle. The timing cycle is positively initiated by the action of the same switch used to break the circuit to the solenoid assembly. When this double pole, single throw switch is thrown, a circuit is completed through the relay actuating the timer at the same instant the slide bar is released by the deenergized solenoid. Drop time for the slide has been accurately determined to be one tenth of a second. It is therefore necessary to correct each recorded time accordingly. The timer used in the timing system is an AC synchronous-motor-driven, DC clutch-circuit type elapsed time indicator. It is calibrated to read to an accuracy of one hundredth of a second. In this type of timer, a timing motor is in continuous operation from a 110 volt AC source. A clutch mechanism which engages the timer hands to the timing motor is driven by 24 volts DC.

There are several critical points in the overall timing system. They are the fine copper wire, its function, and the necessarily sensitive relay. The fineness of the wire is dictated by the limited space available in the very small sample tube. It must therefore possess excellent electrical conductivity as an inherent property. The wire

used in this case is typical of that used in solenoid and relay coils. To perform effectively its function of completing a circuit through the bath medium, care must be taken to insure that the wire is clean and free of oxide coating. The obvious limitation which the size of the wire imposes on current flow requires utilization of a very sensitive relay. The relay used in this case is a 10,000 ohm, normally-closed single-contact type. Current required to actuate the relay is approximately 2.4 milliamps.

Temperature recording system:

Frequent reference has been made in the preceding sections of this report regarding the methods employed in past studies to determine the temperature at which ignition or detonation occurs. The essential objection the writer has to these methods pertains to the fact that bath temperature is that which is recorded and assumed to be acceptable as sample temperature. Both the method and the assumption appear unnecessary to this writer. Thus an important aspect of this study is to produce a method of securing a more reliable indication of sample temperature. To accomplish this, it was decided to make use of a thermocouple placed directly in the explosive sample. A chromel-alumel No. 28 B & S gage thermocouple is used in conjunction with a Fisher Recordall. The Fisher instrument automatically balances and calibrates the thermocouple potential, alleviating the necessity for supplementary cold junction compensation. The temperature history of the explosive sample is thus recorded on the moving calibrated chart.

The relative dimensions of the sample tube, the [illegible] section of the thermocouple, and the sample are such that the temperatures indicated by the thermocouple are representative of those experienced by the sample

particles. That is, the thermocouple contacts both the tube wall and sample particles and is not therefore subjected to heat transfer effects as would be the case if the sample were to completely surround the thermocouple. See Appendix V.

The overall response characteristic of the thermocouple-Fisher Recordall combination was determined to consistently record temperature with less than one-tenth of a second lag and an accuracy of plus or minus one percent.

Operating procedure:

Prior to conducting a series of determinations, the samples are prepared in the following manner: One end of the sample tube is sealed by momentary application in a wing top bunsen burner flame. Loading is accomplished by inserting the open end of the sample tube into a small mound of the explosive to be tested. The tube is inverted and the portion of the sample that has been retained in the open end is shaken to the bottom of the tube. A weight determination is made on the first sample. Subsequent samples may be loaded with sufficient accuracy based on visual comparison of depth of sample in the tube.

When all samples have been prepared, a preliminary equipment check should be carried out to insure proper operation of all components. The steps for this phase of the procedure are as follows:

(a) Timing system (Appendix VI)

(1) Throw control switch to timer position; timer will operate if relay is in normally closed position.

(2) Touch the relay actuation wire to any ground potential; if properly functioning, the relay contact will open, thus stopping timer.

(3) Return control switch to OFF position; reset timer to zero.

(B) Temperature recording system (Appendix VII)

(1) Insure that Fisher Recordall is receiving power and chart is running.

(2) Connect thermocouple leads to recordall, yellow lead to + terminal, red lead to - terminal for proper polarity.

(3) Apply low heat to thermocouple; observe proper operation of recorder.

(C) Solenoid system (Appendix V)

(1) Throw control switch to COIL position; slide bar will be held in upward position.

(D) Heat source

(1) Insure desired heat gradient is available by checking voltage input to heating coils in accordance with Appendix IV.

Following the equipment checks, proceed with determination as follows:

(1) Insert thermocouple and copper relay wire into loaded sample tube. Insure thermocouple is completely embedded in sample.

(2) Insert sample tube in mounting jack, and attach latter to slide bar.

(3) Throw control switch to COIL position, placing slide bar in upward position.

(4) Align immersion assembly over sample tube well.

(5) Throw control switch to FIRE position.

(6) After detonation occurs, observe and record time and temperature.

(7) Return control switch to COIL position; retract slide bar and sample tube assembly.

(8) Remove any bath salts adhering to thermocouple by immersing latter in water. Dry thoroughly prior to reuse.

(9) Repeat steps one through nine for subsequent test runs.

4. Experimental data.

Using the procedure described above, the lowest explosion temperatures were determined for the explosives listed in Appendix VIII. The explosion times at a number of temperatures were also obtained for these explosives. No attempt was made to differentiate between ignition and explosion.

These data were obtained primarily for the purpose of analysing the effectiveness and reproducibility of the equipment design and procedures. Since there were no previous studies that utilized the method employed here for obtaining temperature, no direct comparison can be made with the data from past studies to ascertain and evaluate accuracy of the results obtained. However, data from the sources indicated have been included for the purpose of general comparison and correlations upon which conclusions may be drawn.

In the process of obtaining the data it became evident that the Fisher Recordall chart speed was insufficient when ignition occurred in very short time intervals. Specifically, in those cases where delay time was less than two seconds, the recorder failed to produce a consistently discernible break or variation in the chart trace at the point of ignition. It is therefore necessary to break the trace manually at the instant ignition is observed by throwing the function selector switch on the Recordall control panel from TC (thermocouple) to EXT.

This problem, though considered insignificant for general determinations, is readily alleviated by utilization of an alternate procedure incorporated in the design for the purpose of obtaining a temperature trace versus time on a more precise and higher chart speed device such as a Brush Instrument Co. pen recorder or the Minneapolis-Honeywell Visacord. Examples of data obtained from both instruments are shown in

Appendix I. In this alternate method (see Appendix V), a small coil has been mounted in such a manner as to be centered directly below the slide bar. An alnico rod magnet mounted in the base of the slide bar penetrates the coil as the slide bar descends. This penetration induces a voltage in the coil which is transmitted to one channel in the recording device. A deflection is produced which represents the initial point in the time interval. The thermocouple leads are led to another channel in the recording device providing a temperature trace. Cold junction compensation is of course necessary in this system. Sample ignition induces a thermocouple channel deflection which is sufficient to indicate the time interval termination in addition to pin-pointing ignition temperature. Though not anticipated, it can be observed that an initial time deflection is also induced in the thermocouple channel as the thermocouple falls past the coil.

5. Discussion of results.

The data reported in Appendices VIII and X indicate a degree of consistency and reproducibility sufficient to justify a conclusion that the apparatus and procedures described are acceptable for obtaining information on relative sensitivity of explosives to thermal initiation. In Appendix X the data are presented graphically. In support of the conclusion stated above, it can be seen from the graph that the logarithmic relationship between the time lag prior to explosion and the reciprocal of the absolute temperature results in a straight line for the explosives tested, as required by the equation derived in Appendix II:

$$\log t = A/RT_o + B$$

As pointed out in references (4) and (5), it is widely accepted that an explosion is preceded by a relatively slow reaction which increases more or less rapidly to the detonation point. Though the exact mechanism involved is not fully understood nor agreed upon, the foregoing equation is generally accepted as applicable.

In the specific applications made in most studies however, the log t expression relates to the time lag prior to explosion after heating to a temperature T_o. As pointed out, there is inherent in these applications the assumption that heat transfer is instantaneous. Preliminary tests conducted by the writer using copper blasting caps should indicate a gradient due to heat transfer does exist, and furthermore is not instantaneous as is shown by the calculations in Appendix XI. Time did not permit sufficient experimental investigation to establish the exact magnitude of the gradient involved. It would be expected, as distribution is more pronounced with glass. Referring to the temperature

traces shown in Appendix IX, there is a marked heat transfer effect indicated and the actual temperature of ignition is in both cases appreciably below the temperature of the bath. Insofar as the method employed by this writer is concerned, it may be concluded that bath temperature is not an accurate measure of the temperature of the explosive sample at the time of ignition.

Comparing the data in Appendix VIII, variations between the writers results and those from reference (5) are essentially restricted to differences in recorded temperatures; those of the writer are consistently lower in magnitude.

Further investigation of the heat transfer question when copper tubes are used is necessary before a conclusion can be formed with respect to the relative accuracy of the writer's method versus others.

BIBLIOGRAPHY

1. Davis, T. L., Chemistry of Powder and Explosives, John Wiley & Sons, 3rd edition, pg 21 (1953).

2. Robertson, A. J., Trans. Faraday Soc., 44, 977 (1948).

3. Yoffe, A. D., Proc. Royal Soc. (London), A 208, 488 (1951).

4. Cook, M. A., The Science of High Explosives, Reinhold Publishing Corp., 1958.

5. Henkin, H. and McGill, R., Rates of Explosive Decomposition of Explosives, Ind. Eng. Chem., 44, 1391, June 1952.

6. Liquid Metals Handbook, NavExos P-733(rev) June 1952.

APPENDIX I

DEFINITION OF SYMBOLS

A	Activation energy
B	Constant
C	Heat Capacity
e	2.7183
F	Heat loss (Δ F-free energy of activation)
f	Order function
G	Heat accumulation
H	Heat generated by reaction (Δ H-heat of activation)
h	Planck's constant
K	Thermal conductivity
k'	Specific reaction-rate constant
Q	Heat of explosion
R	Gas constant
ρ	Density
S	Entropy (Δ S-entropy of activation)
T_o	Absolute temperature
t	time (total reaction time)

APPENDIX II

DERIVATIONS

This appendix, taken largely from reference (4) is concerned with the derivation of the equation for the relationship governing the time lag t, prior to explosion upon heating to a temperature, $T_o(^oK)$.

From the heat balance equation

$$K\nabla^2 T + \rho C dT/dt = \rho Q k' f \tag{1}$$

or in simple form

$$F + G = H \tag{2}$$

which in the adiabatic case becomes

$$H = Qk'f = CdT/dt = G \tag{3}$$

integrating to determine parameters,

$$k' = kT/h(e^{-\Delta F/RT}) \text{ and } \Delta F = \Delta H - T\Delta S \tag{4}$$

thus, rewriting equation (3)

$$\int_{t_o}^{t} dt = \frac{Che^{-\Delta S/R}}{QkF} \int_{T_o}^{T} e^{\Delta H/RT} \frac{dt}{T}$$

$$\int_{t_o}^{t} dt = -\frac{Ch}{QkF} \left\{ \int_{x_o}^{x} e^{x} x^{-1} dx \right\} e^{-\Delta S/R} \tag{5}$$

$x = \Delta H/RT$, integrating gives

$$t - t_o = -\frac{Che^{-\Delta S/R}}{QkF} \left\{ \ln \frac{\Delta H}{RT_o} + \frac{\Delta H}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right) + \cdots \right\} \tag{6}$$

let $t = t - t_o$ and assume $T \simeq T_o$ over the interval $t - t_o$, one may consider x^{-1} to be sufficiently invariant to e^x that it may be removed from under the integral. Thus

$$t = -\frac{Che^{-\Delta S/R}}{QkF} \frac{RT_o}{\Delta H} e^{\Delta H/RT_o} \tag{7}$$

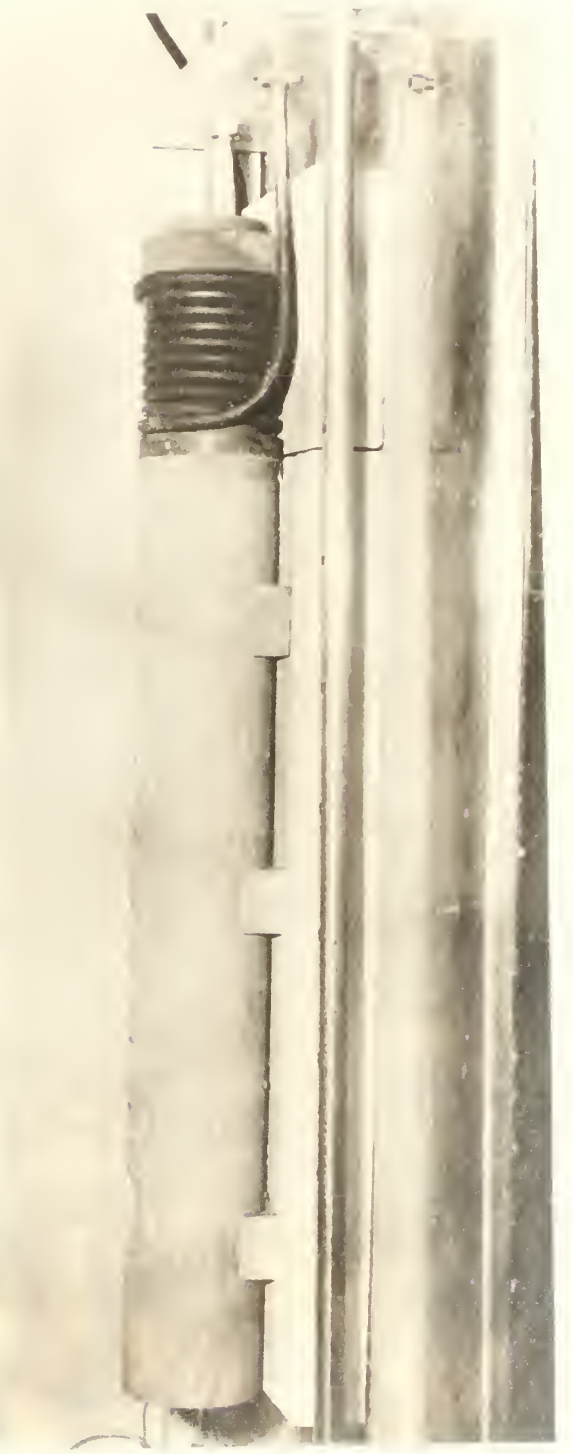
Hence,

$$\log t = A/T_o + B \tag{8}$$

where $A = \Delta H/4.567$ and $B = \log(Che^{-\Delta S/R})RT\sqrt{2}/Q\Delta H$

APPENDIX III

HEAT BAR



APPENDIX IV

VOLTAGE-TIME GRADIENT TABLE

AC VOLTAGE	65	60	55	50
		TIME IN MINUTE °C		
BATH NO.				
1	525	470	410	340
2	510	455	395	330
3	495	445	380	320
4	480	430	370	312
5	465	420	355	301
6	450	410	338	290
7	440	400	330	280
8	430	390	345	272
9	420	380	340	265
10	415	375	335	260

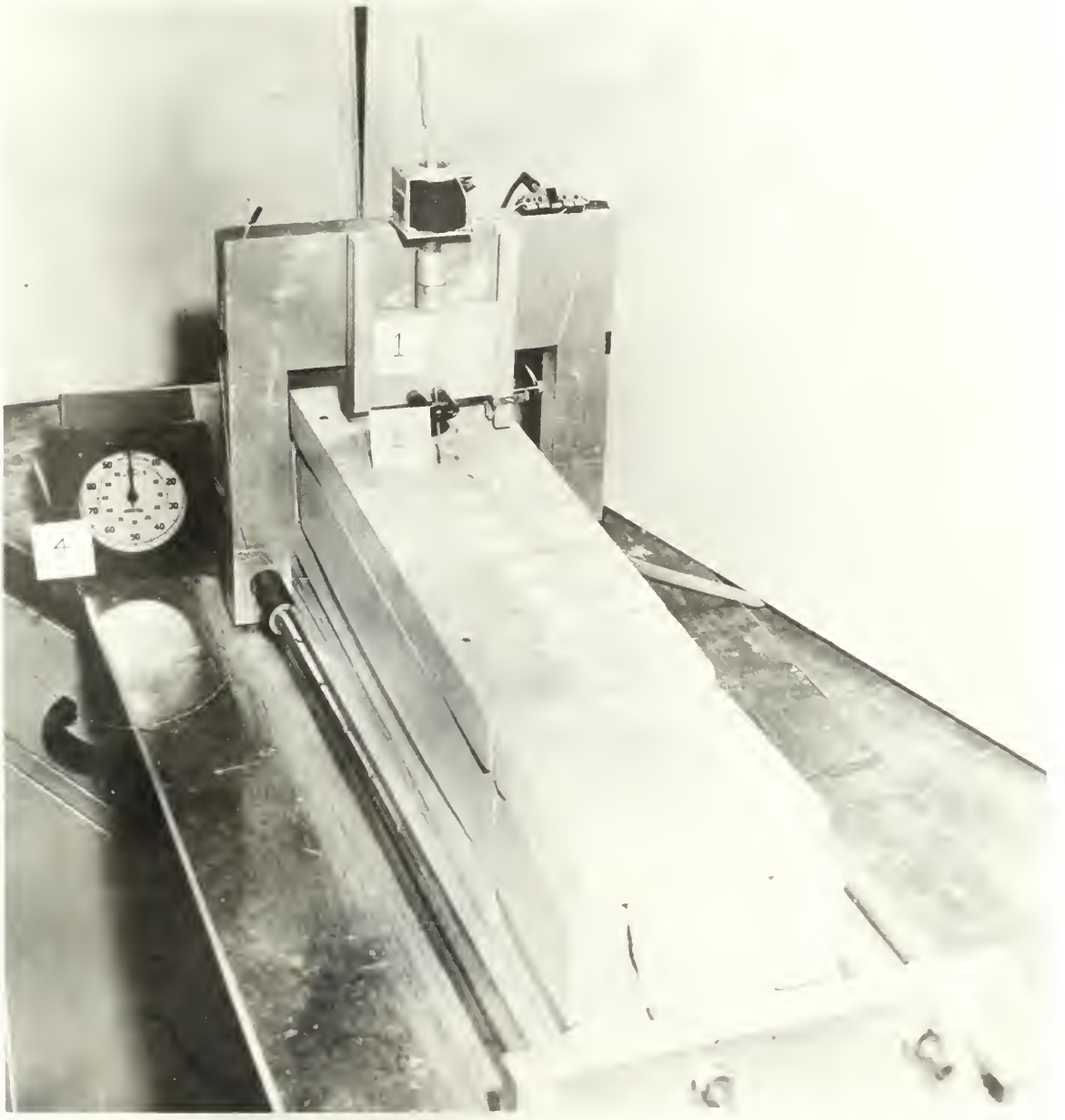
APPENDIX

1 2

1. TUBE MOUNTING JACK
2. SAMPLE TUBE

APPENDIX VI

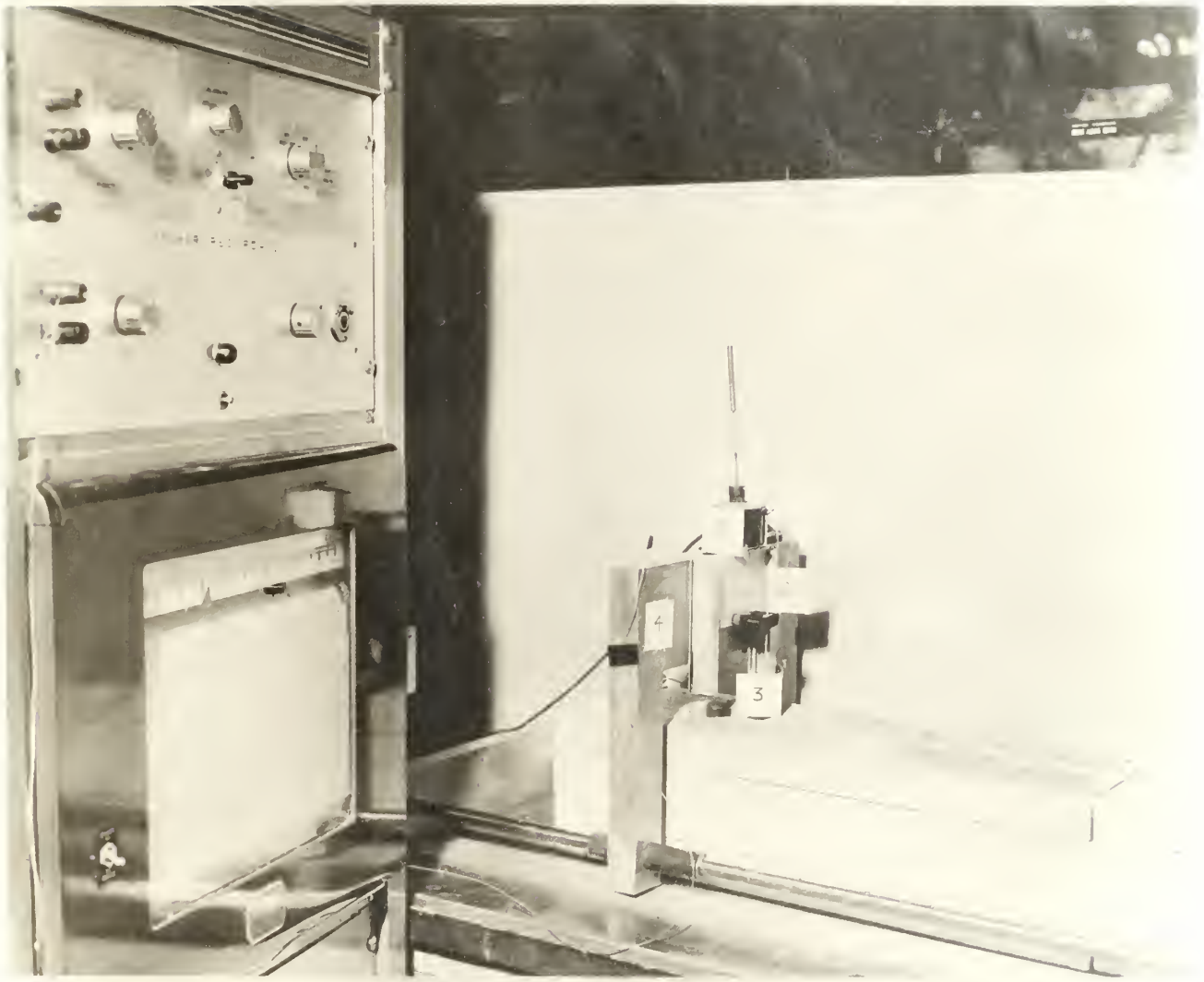
TIMING SYSTEM



1. SLIDE BAR
2. SAMPLE TUBE
4. TIMER

APPENDIX VII

TEMPERATURE RECORDING SYSTEM



1. SOLENOID
2. SLIDE
3. SAMPLE TUBE
4. SUPPORT

APPENDIX VIII

TEST DATA

In this appendix the writers results are listed with comparable data from reference (5) for comparison purposes.

LEAD STYPHNATE

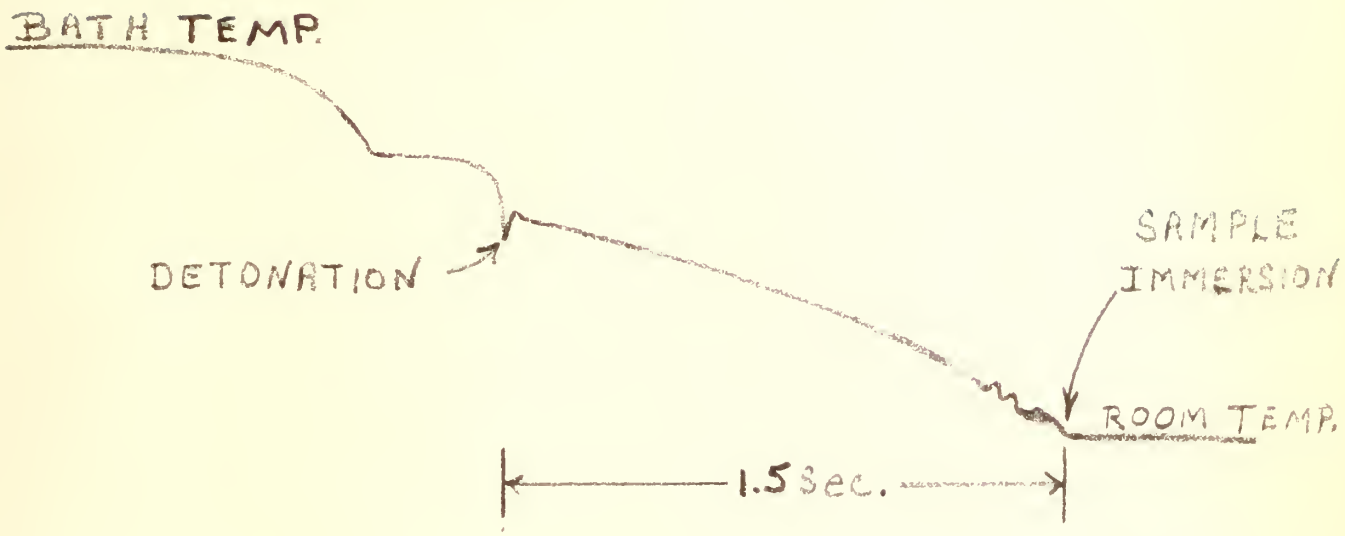
Writers Data		Reference (5)	
Temp. °C	Time(sec.)	Temp.°C	Time(sec.)
316	0.36	323	0.56
292	1.59	315	1.79
273	1.82	301	4.47
250	12.60	294	9.62
239	25.20	288	15.60
Activation Energy (KCal/g.mole,°K)			
33.5		58.8	

PETN

325	0.49	350	0.050
296	0.66	272	0.475
275	1.40	256	1.03
252	1.86	244	1.57
224	4.02	220	4.56
Activation Energy (KCal/g.mole,°K)			
15.9		22.0	

APPENDIX IX

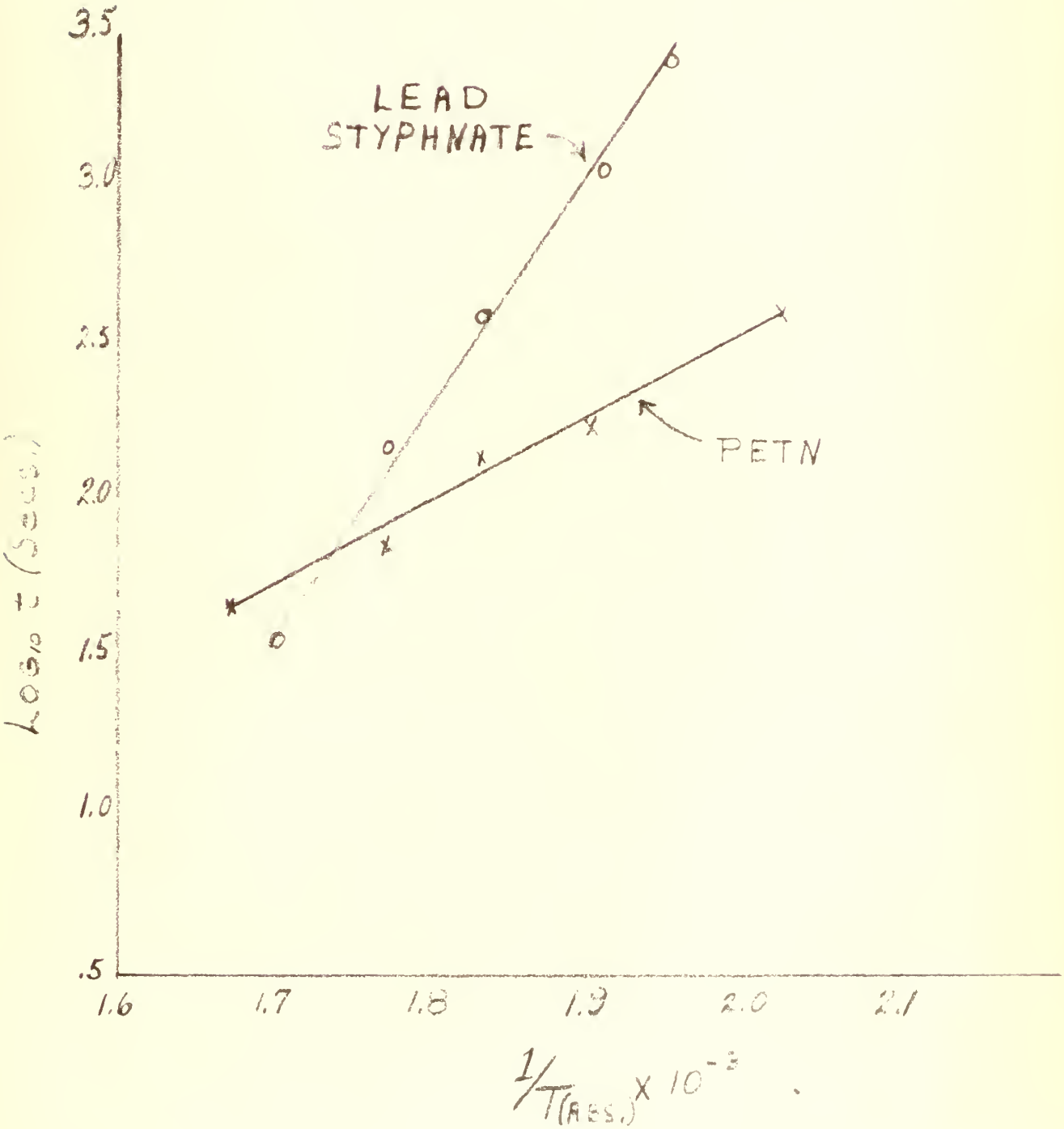
TEMPERATURE TRACE



MINNEAPOLIS-HONEYWELL VISACORD

BRUSH PEN RECORDER

APPENDIX X


3.5
3.0
2.5
2.0
1.5
1.0
.5
LEAD STYPHNATE
PETN
1.6
1.7
1.8
1.9
2.0
2.1
1/T(ABS.) X 10⁻³

APPENDIX XI

HEAT TRANSFER CALCULATION

This appendix is concerned with the calculation of the time required for heat transfer in a Woods metal bath-copper sample tube system. The calculations are based on a bath temperature of 300°C as a representative average of the temperature range covered by the experimental data of references (1) and (5). Representative values of film coefficient (h) were obtained from reference (6).

Formulating a heat balance for the system

$$A \Delta t \rho C_p \frac{dt}{d\theta} = A h (T_b - T_i)$$

recognizing that T_i will never actually reach the value T_b, assume the upper limit of integration to be T_b-10°. Separating variables

$$\int_{T_i}^{T_b-10} \frac{dT}{T_b - T_i} = \frac{h}{\Delta t \rho C_p} \int_0^{\theta} d\theta$$

integrating, one obtains

$$-\ln \frac{[T_b-(T_b-10)]}{[T_b-T_i]} = \frac{h}{\Delta t \rho C_p} \theta$$

solving for θ gives

$$\theta = \frac{\Delta t \rho C_p}{h} \ln \frac{[T_b-T_i]}{[T_b-(T_b-10)]}$$

applying various values of (h), leads to the following:

h	1700	2000	2300	2600
θ sec)	0.308	0.262	0.228	0.175

where

T_b Bath temperature
T_i Initial temperature of copper tube (room temp. 70°F)
Δt Thickness of copper tube (.00067 ft.)
ρ Density of copper (556 lbs/ft^3)
C_p Specific heat of copper (.01 Btu/lb,°F)
h Film coefficient(Btu/lb, ft,^{2} °F)
θ Time involed in heat transfer